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# Quantification of Release of Critical Elements, Formation of Fly Ash and Aerosols: Status on Current Understanding and Research Needs

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## ABSTRACT

Deposit formation in utility boilers occurs via a number of consecutive steps; [1)] release of critical elements like K, Na, Pb, Zn, S and Cl, [2)] formation of gaseous species, fly ash and aerosols, [3)] transport and adhesion of ash species, [4)] deposit build-up and consolidation, and, finally, [5)] shedding of deposits. Some of the steps may be repetitive, as the process is partly cyclic [Frandsen, 2011].

The inorganic fraction of solid fuels, may cause several problems during combustion, most importantly formation of particulate matter (aerosols and fly ashes). These may subsequently induce deposit formation (slagging and fouling) on superheater tubes, leading to a potential reduction in heat transfer efficiency to the water/steam cycle, or, to chemical attack (corrosion) or physical wear (erosion) of superheater tubes. These problems may give rise to irregular operation, or even costly shutdowns of combustion units.

Through several years, high quality research has been conducted on characterization of fuels, ashes and deposit formation in utility boilers fired with coal, biomass and waste fractions. Huge amounts of experimental data have been reported, from such work, but the fact is that there are still in 2017, a number of big gaps in our current understanding of these phenomena, and that we need focus on these points, in order to be able to describe, understand, and, quantify the processes of ash and deposit formation completely [Frandsen, 2009].

This paper provide a brief outline of the current status on release of critical ash-forming elements, formation of aerosols respectively fly ash formation is systems fired with solid fuels. The paper is a significantly updated, but condensed version of a review-paper on the same subject, presented in Lapland, Northern Finland in 2010 [Frandsen et al., 2010].

## 1. INTRODUCTION

A lot of high-quality data are available on the release of critical ash-forming elements, although most of the lab-scale measurements are performed under experimental conditions, quite different from what happens in full-scale, the main difference being the particle size distribution of the fuels investigated, and the time-temperature history, mainly the heat-up rate and final temperature experienced by the fuel particles. Nevertheless, several good attempts have been made to derive mechanisms for the release of especially K, S and Cl, taking into account chemical interactions with other elements like Al, Si and Ca. But, there is still a lack of fundamental understanding, before we can perform a reasonable quantification of the release of critical ash-forming elements and species from single particles in suspension, or beds (fixed or fluidized) of burning fuels. We are in other words still pretty far away from being able to provide reliable boundary conditions for e.g. advanced flow models, in order to simulate freeboard chemistry, aerosol modeling and heterogeneous condensation etc., in these systems, as also indicated by [Hansen et al, 2017a,b].

A lot of focus has also been put on aerosol formation, mainly via a significant number of measuring campaigns reported in the literature. We have a good qualitative image, and understanding, of mechanisms of aerosol formation, and for some fuels even 1st generation models for aerosols formation have been formulated. Aspects of aerosol transport have also been addressed thoroughly in the literature, but in this case there is a big gap to step over, before these models are fully implemented in e.g. models for freeboard chemistry or advanced flow in furnaces.

Concerning fly ash formation, this is well described for coal-firing in suspension, where reliable models for prediction of final chemistry and particle size distribution have been published and tested, while for utilization of other fuels, the physical description of how the residual ash is formed is still unknown territory, basically. The physical development of fly ash link to the fate of this ash, further down the line in the actual combustion system [Frandsen, 2011];

- Will it be lifted from the fuel-bed ?
- Will it be transported to the heat transfer surfaces, and in case yes, where will that happen ?
- Will it stick to a heat transfer surface upon impact ?
- How will it transform and/or interact with e.g. gaseous species during transport up through the freeboard etc. ?

Often, we have lots of bulk chemical analyses of fly ash particles that have been collected in various positions, but there is a lack of physical understanding, and detailed investigation, of how these particles actually develop, during the thermal fuel conversion process.

Thus, fly ash formation has through several decades been intensively studied for coal combustion, where the fly ash size distribution has a multi-modal size distribution, see Figure 1. The larger particles originate from mineral grains in the coal, and their size distribution depends upon the coal characteristics, pre-treatment (sizing) of the coal, and,

the actual combustion conditions. The submicron particles on the contrary, originate mainly from homogeneous nucleation, and subsequent coagulation of flame-volatilized inorganic species, see Figure 1. Other important processes going on include fragmentation of chars and mineral inclusions as well as coalescence of ash droplets on receding char surfaces [Flagan and Friedlander, 1978].

The residual ash formed during thermal conversion of fuels, may be further subdivided into bottom ash and fly ash, in a ratio depending mainly on fuel characteristics, furnace design, and size and density of the residual ash particles formed. In grate-fired units, the major part of the residual ash ends up as bottom ash (app. 70-95%), whereas in pc/pf-fired boilers, fly ash constitutes the main part of the residual ash (80-95%).

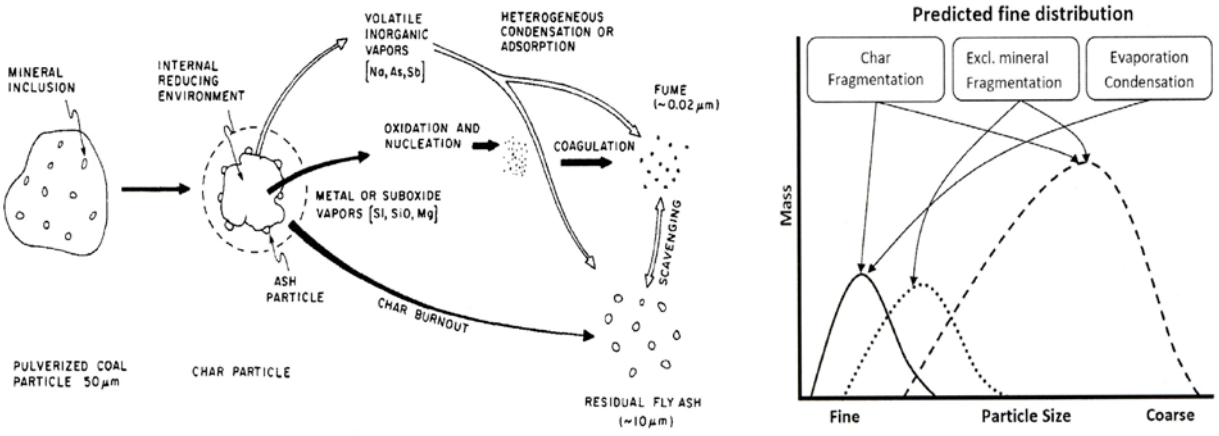



**Figure 1:** Major transformation routes and transformation processes from a burning solid fuel to a fly ash particle size distribution. Source: [Haynes et al., 1982; Vejahati et al., 2010]

The main route between a burning fuel particle in a furnace, and a troublesome deposit on a heat transfer surface, can be divided into a number of consecutive steps [Benson et al., 1993; Frandsen, 2011]:

- **Release** of critical ash-forming elements (mainly K, Na, S, Cl, Zn, and Pb) during devolatilization, pyrolysis, and subsequent char burnout;
- **Formation of aerosol particles** by nucleation and coagulation of flame-volatilized ash-forming elements, and, formation and entrainment of **residual (fly) ash** (during char burnout);
- **Transport** of ash species i.e. gases, liquids (droplets) and solids (particles), from bulk gas to heat transfer surfaces, and, adhesion of these ash species to heat transfer surfaces, and;
- **Build-up**, **sintering** (consolidation), and, **shedding** of deposits.

Below, an introduction to the current understanding on release of critical elements, formation of inorganic aerosols and (residual) fly ash, is provided. An attempt is made to

pinpoint gaps in the underlying data and understanding, explaining mechanisms and the ability to model these processes.

## 2. RELEASE OF CRITICAL ASH-FORMING ELEMENTS

Several factors are known to influence the release and retention of elements and ash species, during combustion of solid fuels [Knudsen, 2004; Knudsen et al., 2004a,b, 2005; Van Lith, 2005; van Lith et al., 2006, 2008; Novakovic et al., 2009];

- First of all, the combustion temperature correlates strongly with the fraction of critical ash-forming elements (K, Na, S, Cl, Pb, and Zn) released.
- Secondly, *in coal combustion* the release of ash has been shown to be affected significantly by the oxidizing/reducing conditions during thermal conversion of the coal particles. The reducing conditions e.g. inside burning coal char particles, may increase the vaporization of certain ash-forming elements, since the reduced form (sub oxide) of many oxides of ash forming elements have higher vapor pressures, than the corresponding oxides [Senior and Flagan, 1982].
- Third, the fuel composition affects the release. For biomass fuels several composition-dependent relations have been identified [Knudsen et al., 2004a,b; van Lith et al., 2006, 2008, Novakovic et al., 2009].
- Fourth, the fuel particle size and structure and temperature-residence time history also affect the measured release rates [Flagan and Seinfeld, 1988; Knudsen et al., 2004a,b].

As an example, during wood-firing on a grate, the release of K seems to start around 500–600 °C for spruce, beech, and bark, whereas for fibre board small fractions of K (~10%), may be released even below 500 °C, due to release of organically associated K, during thermal degradation of the organic structure in the devolatilization stage [Davidsson et al., 2002 a,b,c]. Carboxyl groups also start to decompose, at relatively low temperatures (<300 °C), meaning that during pyrolysis, atomic-K, will be released mainly by the following mechanism [van Lith et al., 2008]:

$$Char - COOK \rightarrow Char + CO_2(g) + K(g) \quad (01)$$

However, at temperatures < 600 °C, phenol groups are still present in the char, which may rebind some of the released atomic-K, may be bound to those groups in the char [van Lith et al., 2008]:

$$Char - C_6H_5 - OH + K \rightarrow Char - C_6H_5 - OK + H \quad (02)$$

Above 800 °C, decomposition of $K_2CO_3$ is the dominant mechanism of K-release observed for spruce, beech, and bark. Thermodynamic equilibrium calculations indicate that the decomposition of $K_2CO_3$ starts above 800 °C, while thermogravimetric analysis and differential thermal analysis of wood ash indicate that the dissociation of $CaCO_3$ and $K_2CO_3$ takes place at 700–900 °C, depending on the wood type [Misra et al., 1993]. Decomposition of $K_2CO_3$ may form K(g), according to eqn (03);

$$K_2CO_3 \rightarrow 2K(g) + CO_2(g) + ½O_2(g) \quad (03)$$

K(g) released may react further with other species present in the gas phase, e.g. $H_2O(g)$ thereby forming KOH(g). In the presence of HCl(g), conversion to KCl(g) is more likely.

Figure 2 shows that the biofuels investigated by [Knudsen, 2004], can be divided into two groups, based on their K-release pattern, above 800 °C.

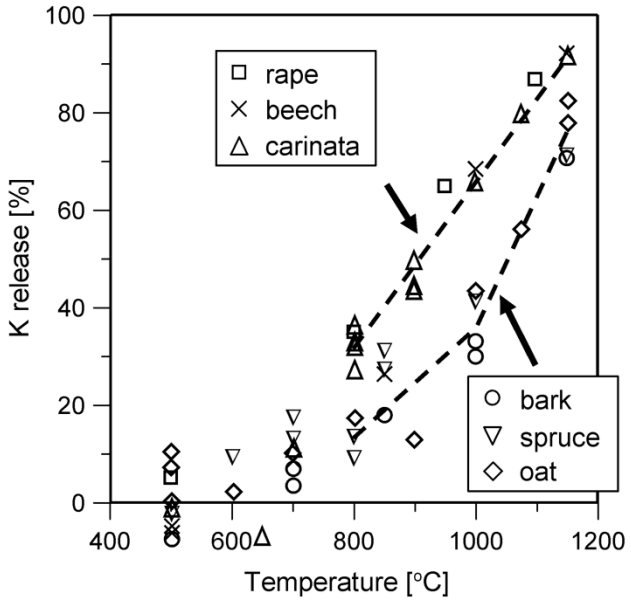



**Figure 2:** Comparison between the release of K from wood fuels and Cl-lean annual biomass fuels. Source: [Knudsen et al., 2004a; van Lith et al., 2008].

The main mechanisms for transformations and release of organically associated K and KCl, during pyrolysis and combustion, are summarized in Figure 3.

Chlorine-release is way more complex than K-release. Reactions of KCl with organic species, forming $CH_3Cl$ and HCl is the main mechanism for low-temperature Cl-release (< 500 °C). Part of the organic-Cl, may also be directly release during pyrolysis. At higher temperatures, vaporization of KCl become a more important mechanism. The process is sensitive to temperature (especially > 700 °C), and might be diffusion limited.

During char burnout, the organic structure disintegrates, thereby bringing the silicates in the outer structure of e.g. straw in closer contact with retained K and Ca, primarily hosted in the center matrix of an organic structure. Metal-silicate reactions may therefore enhance the release of Cl, as K seems to prefer association with silicates, rather than chlorides.

Recapture of HCl by char-K might also be of importance under fixed-bed conditions, especially with a thick char bed.

Figure 4 summarizes the findings on the topic of Cl-release during biomass combustion.

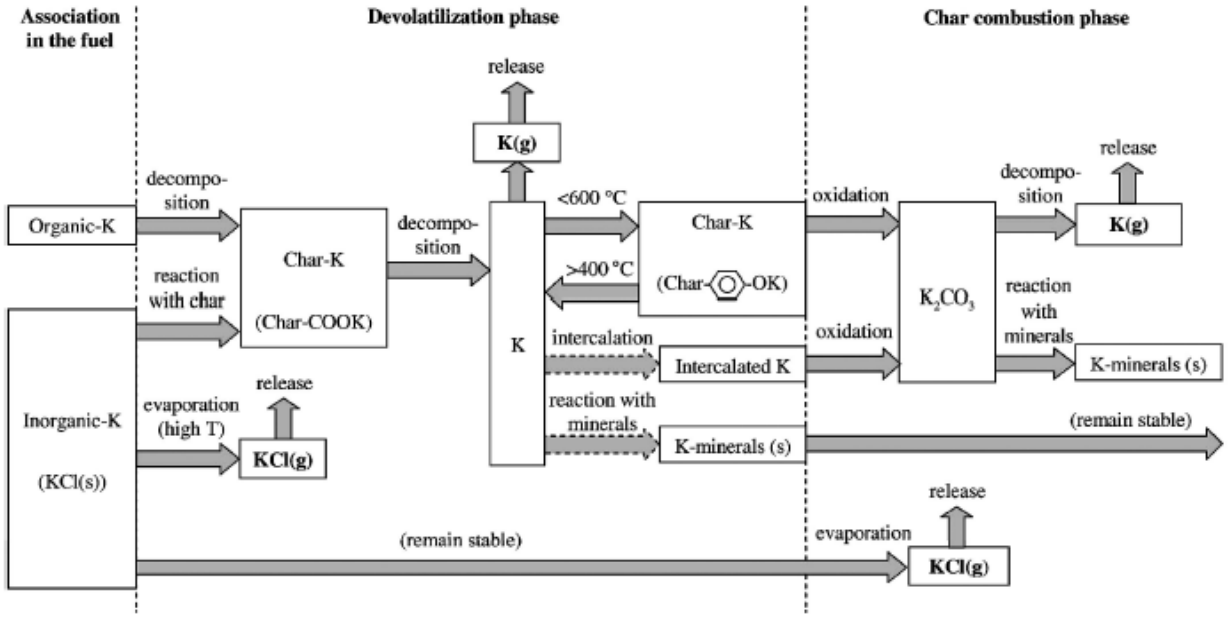



**Figure 3:** Possible transformations and release mechanisms of organically associated K and KCl during devolatilization and combustion of biomass. Source: [Johansen et al., 2011].

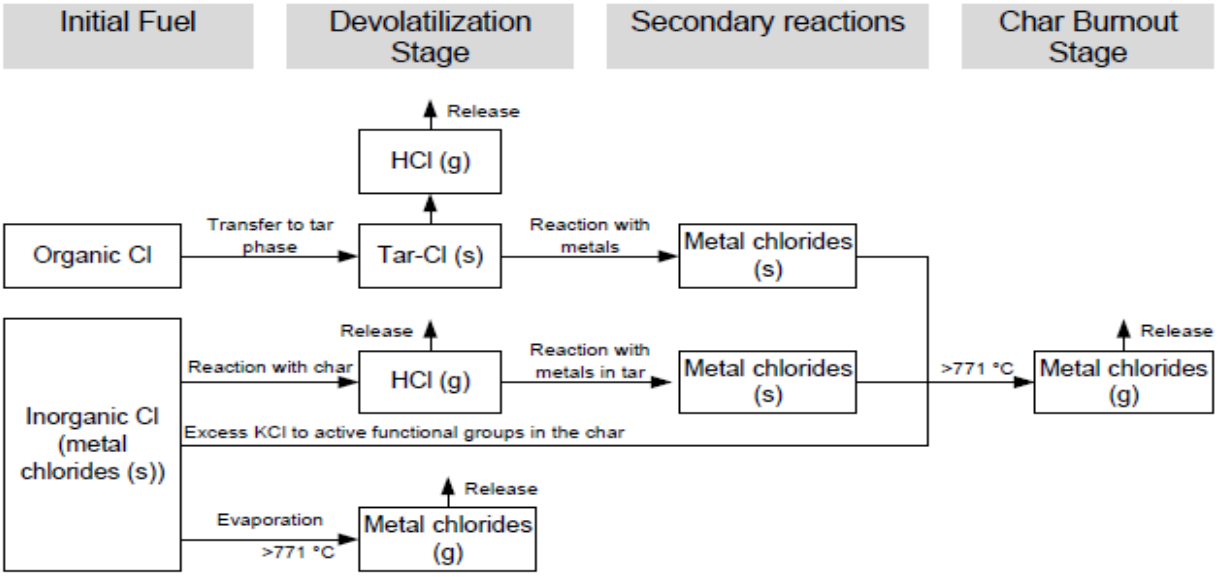



**Figure 4:** Possible reaction paths and release mechanisms of chlorine during devolatilization and combustion. Source: [Johansen et al., 2011].

Figure 5 summarizes the possible reactions and release mechanisms for S, during combustion of biomass. The S-transformations are a complex matter, including both organic and inorganic relations, as well as a series of complex secondary reactions.

Concerning phosphorus, [Wu et al., 2011] studied the release and transformation of K, Na, P, S and Cl, during grate-firing of bran [a P-rich residue from the milling of wheat grain, used for the production of ethanol] in a fixed-bed, laboratory-scale reactor, and found that K, P, S, and to a lesser extent Cl and Na, were released to the gas phase. Sulfur was almost fully vaporized during pyrolysis, below 700 ˚C; while ~ 60-70 % of K and P in bran, were released during combustion, in the temperature range 900-1100 ˚C.

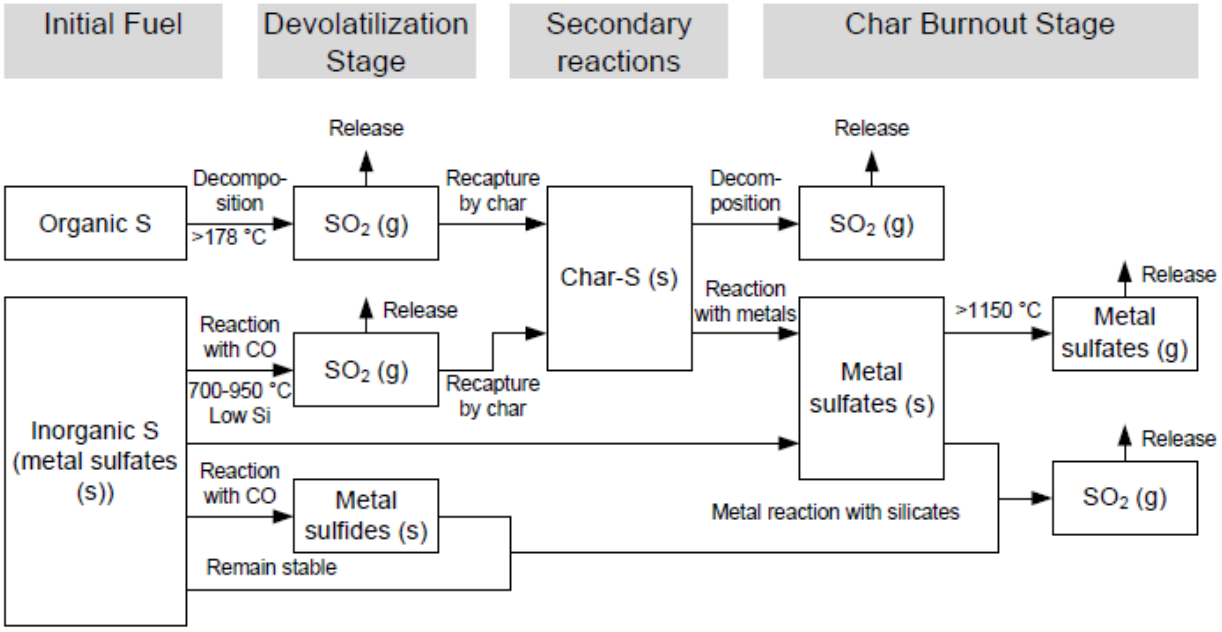



**Figure 5:** Possible reaction paths and release mechanisms of S during devolatilization and combustion. Source: [Johansen et al., 2011].

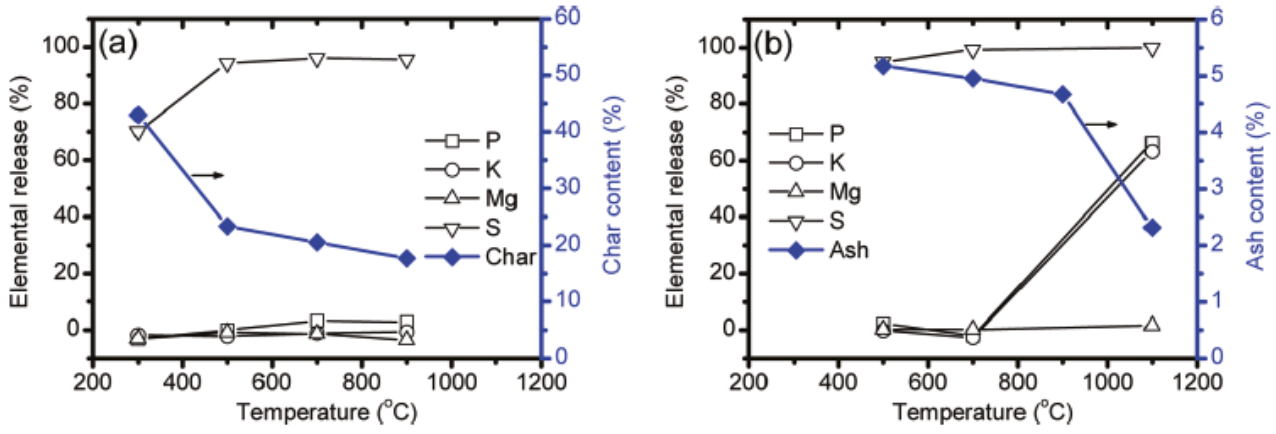
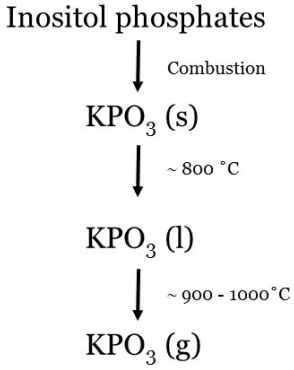



**Figure 6:** (a) Release of P, K, Mg, and S, and the char content of bran at different temperature during pyrolysis. (b) Release of P, K, Mg, and S, and the ash content of bran at different temperature during combustion. Source: [Wu et al., 2011].

The P-release was presumably due to vaporization of $KPO_3$, generated from thermal decomposition of inositol phosphates [a group of mono- to poly-phosphorylated inositols, playing a crucial role in cellular functions], a major source of P and K in bran [Wu et al., 2011].

When bran is combusted at high temperature, P in phytic acid/phytate may be transformed to phosphorus oxides/phosphates; thus the vaporization of P, Mg, and K in combustion depend to a large extend on the vapor pressure of the phosphorus oxide/phosphates [Wu et al., 2011].

Release of P, K, and Mg, was found to be negligible up to 900 ˚C, implying that these elements in bran, are not associated with the volatiles released during pyrolysis, and that the inorganically associated or char bounded P, K, and Mg, are rather thermally stable, up to 900 ˚C. From Figure 6b, it can be seen that the release of P, K, and Mg is negligible at combustion temperatures of 500 and 700 ˚C, whereas the release of S is almost complete, in agreement with the pyrolysis results, see Figure 6a.




The data suggest that during char combustion, organically associated P, K, and Mg in bran are most likely transformed to stable inorganic species, which are not vaporized < 700 ˚C [Wu et al., 2011].

According to the results shown above, the primary release mechanism of P and K during bran combustion is proposed in Figure 7. During combustion, the inosital phosphates in bran may be converted to $KPO_3$.

**Figure 7:** Proposed primary release mechanism of P and K during bran combustion. Source: [Wu et al., 2011].

At temperatures around 800 ˚C, $KPO_3$ may be molten. When the temperature is increased to 900 - 1100 ˚C, vaporization of $KPO_3$ happens, releasing P and K to the gas phase. This proposed mechanism is supported by several experimental observations [Wu et al., 2011];

- First, the residual ash from bran combustion is melted in the temperature range 700 - 900 ˚C, which is consistent with the melting temperature of $KPO_3$, and;
- Second, the release of K and P during bran combustion happens in the temperature range 900 - 1100 ˚C, which is also in agreement with the observed vaporization behavior of $KPO_3$.

The influence of additives such as $CaCO_3$, $Ca(OH)_2$, and kaolinite on the release during bran combustion, was also investigated. Ca-based additives generally increased the molar ratio of the released K/P, whereas kaolinite showed the opposite effect.

[Korbee et al., 2010] conducted a study including wood chips, waste wood, olive residue, and straw alongside with a UK and a Polish coal. Coal and biomass were combusted in the ECN Laminar Combustion Simulator (LCS), which is an advanced drop tube furnace, that can be applied to study the behavior of a single or blended solid fuel, under typical pulverized fuel

fired furnace conditions. An oil-cooled, quenched gas/particle probe was used for sampling char and ash at four locations along the reactor vertical axis. The particle residence time was taken to be that of a particle, with an aerodynamic diameter of 50 μm.

It was found that most of the inorganic matter was released in the first ~200 ms of the conversion process, however the release in the last burnout stage (1300 ms) with extended residence time, was still significant. Large differences were observed between fuels. The release expressed in mg/kg db was influenced by the ash content of the actual fuel, and the reactivity of the ash constituents. The relatively low ash release from the wood-type fuels reflects their low ash content, and the high ash release from olive residue and straw was caused by the higher ash content but especially by the high ash volatility. The release from both coals was dominated by the elements sulfur and chlorine. If the sulfur content of the coal is high, then the release will be high, too.

Direct release studies on different fuels in FBCs are more scarce. Anyhow, due to the well-known and -documented interactions of particularly the alkalis with the bed-material in FBCs, a lot of work has been conducted on bed agglomeration and subsequent deposition, data from which indirect information on release of alkalis, S and Cl, may indeed be derived [Valmari et al., 1998; Lind, 1999; Valmari, 2000; Lin et al., 2003].

The Si- and Al-contents are known to be important factors affecting alkali release from burning fuels. There are several studies on the formation of alkali silicates, which are stable and non-volatile under combustion conditions, and thereby inhibit the release of gaseous alkali metals. Aluminum silicates (e.g. kaolin) have been reported to capture alkali metals effectively by chemical reaction (chemisorption), forming alkali aluminum silicates. For other silicates and alumina ($Al_2O_3$) both chemisorption and physical adsorption have been proposed as the capture mechanism [Shadman and Punjak, 1988; Uberoi and Shadman, 1991; Coda et al., 2001]. There is evidence that the presence of fuel alkali earth metals, significantly decreases the retention of alkali metals in the silicate structure, by competition for the ionic positions in silica molecules, indicating the importance of the ternary system including alkali metal, alkali earth metal and silicate for the behavior of alkali metals [van Lith et al., 2008; Novakovic et al., 2009].

In biomass fuels rich in P, an important system for alkali retention might be the formation of (Na,K)–(Ca,Mg)–phosphates [Sandström, 2006; Novakovic et al., 2009;]. These compounds are non-volatile, and therefore decrease the release of alkali metals. They are formed in large quantities when e.g. cereal crops or sewage sludge are burned [Sandström, 2006]. In addition, P-based additives have been utilized successfully to prevent release of alkali metals in straw combustion [Tobiasen et al., 2007; Sippula, 2010]. Secondary reactions between released (alkali) metals and char or ash inclusions in the fixed bed, have also been thoroughly investigated [Novakovic et al., 2009]. For wood-type fuels, the role of P in the secondary interactions between gaseous alkali metal species and residual ash is still unclear [Novakovic et al., 2009].

[Wu et al., 2011] also investigated the reactions between gaseous P and Ca-based additives by mixing $KH_2PO_4$ and $Ca(OH)_2$ at a molar ratio of 1:1, and then heating the mixture to 1500 ˚C, at a rate of 10 ˚C/min, in a high-temperature oven. The mass loss obtained in the experiment was 16,2 %wt, leading to the hypothesis that $KCaPO_4$ is formed during the heating of the mixture, since the vaporization of $KCaPO_4$ is negligible, even at 1500 ˚C. The

result confirms that Ca-based additives affects the retention of P-species, during combustion. Two plausible global mechanisms, depending on whether reaction or thermal decomposition occurs first, were proposed by [Wu et al., 2011];

$$KH_2PO_4 + Ca(OH)_2 \rightarrow KCaPO_4 + 2\,H_2O \quad (04)$$

$$KPO_3 + CaO \rightarrow KCaPO_4 \quad (05)$$

Comparing different Ca-species, it seems that when the same molar ratio of Ca/K is applied, $Ca(OH)_2$ has a more significant effect on the release of K, than $CaCO_3$, which may be explained by the particle size of the $Ca(OH)_2$ and $CaCO_3$ used in the experiments, since the $Ca(OH)_2$ particles were much smaller, compared to $CaCO_3$.

Compared to K, the influence of additives on the release of P, was found to be insignificant. With the addition of Ca-based compounds, almost no reduction in the P-release is observed [Wu et al., 2011].

| **Fuel\Technology** | **Suspension-firing** | **Fixed-bed firing** | **Fluid-bed firing** |
|---|---|---|---|
| **Coal** | ☺☺[1] | *Minor relevance* | ☺ [5] |
| **Annual biomass/ Energy Crops** | ☺☺[1] | ☺☺☺☺ [2] | ☺ [5] |
| **Wood fuels** | ☺☺[1] | ☺☺☺☺ [3] | ☺ [5] |
| **Waste fractions** | ☹ | ☺☺ [4] | ☹ |

**Table 1:** Overview of available data on release of critical elements like K, Na, Cl, S, Zn, and, Pb in different technologies. Several studies of release from annual biofuels and wood fuels have been reported, while there is a lack of release data for waste fractions in suspension respectively fluid-bed firing.
1 – [Korbee et al. 2010], 2 – [Knudsen, 2004], 3 – [van Lith, 2005], 4 – [Pedersen et al., 2010], 5 – Direct studies on release from FBCs are scarce, but a lot of gas phase alkali measurements and bed agglomeration work have been conducted, from which certain aspects of release may be derived.

In the release studies summarized above, it has been shown that increasing temperature, reducing conditions and a high Cl/Me-ratio usually facilitates release of metals (Me) like K, Na, Zn and Pb. On the other hand, a high S-level usually makes condensed sulfates thermodynamically stable, often also at higher temperatures, than what is actual for condensed chlorides. The effect of Si (and Al) seems to be to fix a certain amount of especially the alkalis in condensed phases, thereby increasing the retention of these in the bottom ash fraction.

In summary, fundamental data on release of critical ash-forming elements, especially from fixed-beds are available, see Table 1. The critical parameters, like temperature, fuel (ash) chemistry, local stoichiometry and sample preparation and size, controlling the release, have also been indentified and discussed thoroughly, in the literature. Controlling chemical parameters, like the (K+Na)/Si, or, the (K+Na)/Cl+2S ratios, have at several occasions been proved to correlate well with alkali release. Similar, controlling chemical parameters are not yet available for the heavy elements, like Zn and Pb.

In spite of the high-quality work and effort to quantify release, there is still a major gap in the theoretical quantification of the release, i.e. the ultimate goal, defining boundary conditions for free board chemical and physical processes, for use e.g. in a CFD-frame, is still to be considered a future task. Much more development of single particle release models as well as release from bed/ensembles of particles, and physical entrainment of particles e.g. from a fuel bed, is needed in the future in order to develop reliable quantitative release models for implementation in fuel quality advisors or advanced flow based prediction of ash deposition propensities.

Direct quantification of release from FBCs, or in suspension-fired units, utilizing waste fractions are scarce.

## 3. AEROSOL FORMATION

Fly ash formed during pulverized coal combustion, exhibits at least a bimodal size distribution, see Figure 1. Most of the mass occurs as fly ash particles whose mean diameter is ~ 10 μm. However, most of the surface in the fly ash size distribution, is carried by very fine (~ 0.03 μm) fume particles, even though the fume constitute only a small (but variable, depending on the actual combustion conditions) fraction of the total ash mass. Evaporation of volatile elements, such as As, Na, Cl and S, and subsequent heterogeneous condensation of these volatile elements, in cooler regions of the furnace, may cause surface enrichment of both fume and fly ash particles [Haynes et al., 1982].

As flue gas is cooled, supersaturated vapors can either condense on surfaces of existing particles or form new nuclei. This problem was addressed for pulverized coal combustion by [McNallan et al., 1981], showing that homogeneous nucleation of fine particles of silica may occur at temperatures above approximately 1430 °C, in spite of the presence of preexisting particles. Homogeneous nucleation of particles of $Na_2SO_4$ may occur below 1500 °C, at a cooling rate in excess of 600 °C/s, and, with a 1 g/Nm$^3$ mass loading of existing 8 μm particles. However, if the gas is loaded with very fine particles of silica, caused by homogeneous nucleation at higher temperatures, the number density of particles in the gases would be so high that the $Na_2SO_4$ would condense on these particles, while homogeneous nucleation of $Na_2SO_4$ would be suppressed [McNallan et al., 1981].

Later, [Damle et al., 1982] concluded in a review paper on aerosol formation mechanisms from coal combustion, that the size distribution of particles with $d_P$ < 1 μm, can be qualitatively explained by a vaporization-nucleation mechanism. Alternative mechanisms suggested especially for the formation of fine particles containing Al-silicate matrix elements include; [a)] presence of extraneous submicron particles not associated with coal, such as clays, [b)] mineral inclusions released as submicron particles without coalescence, [c)] bursting of molten ash bubbles releasing fine submicron particles, and, [d)] reduction of matrix elements at the coal particle surface during combustion, producing more volatile species [Damle et al., 1982].

The mechanisms of submicron particle formation and growth, during pulverized coal combustion, were further investigated in a detailed laboratory study by [Helble and Sarofim,

1989a]. Narrowly size-segregated coal samples and synthetic chars, containing a single mineral compound, were burned in $O_2/N_2$ atmospheres at 1480 °C, producing ash which was size segregated and chemically examined. Coalescence of recently nucleated primary particles occurred in these experiments by either solid state diffusion or viscous flow, and was found mainly to be a function of [1)] the gas temperature, and [2)] the chemical composition of the ash particles. The addition of Na to Si-systems was seen to greatly increase the size of the sub micrometer primarily particles, by decreasing the viscosity, and, therefore permitting coalescence at lower temperatures [Helble and Sarofim, 1989a].

Aerosol formation was also studied intensively when co-firing coal and straw in the suspension-fired MKS1 boiler in Studstrup, Denmark [Andersen, 1998]. During mass balance closures for the boiler, aerosols were sampled near the economizer. The overall effect of coal-straw co-firing on the formation of aerosol particles was found to be minor, as the sub micron aerosol particles were generally formed at high temperatures by processes in the burning char, and these reactions were only marginally affected by the introduction of straw to the boiler. Neither number nor mass concentration of submicron particles was significantly increased by coal-straw co-firing in suspension [Nielsen et al., 1996; Nielsen and Livbjerg, 1997].

It was found from the aerosol measurements that K gradually disappears in the submicron particles during coal combustion. Thus, K behaves like a non-volatile species during coal combustion. During co-firing however, K was significantly enriched in submicron articles compared to fly ash, and also an enrichment of K on the surfaces of the larger particles was observed [Nielsen et al., 1996, 1997; Nielsen and Livbjerg, 1997].

A serious amount of high-quality work, has been conducted in order to outline and understand the mechanisms of aerosol formation from solid fuel combustion. For coal combustion, the pioneering work was conducted mainly at MIT, back in the early 1980s, proposing the reduction-reoxidation mechanism, in which non-volatile oxides of e.g. Ca, Mg and Si (e.g. SiO2) are reduced to suboxides (e.g. SiO) or free elements (e.g. Si), having a much higher vapor pressure, thereby evaporating inside the coal char structure where reducing conditions prevail. At the surface of the char, an immediate reaction with $O_2$ occurs, and a fume of oxide nuclei is generated, which will subsequently form an aerosol by coagulation and heterogeneous condensation [Senior and Flagan, 1982].

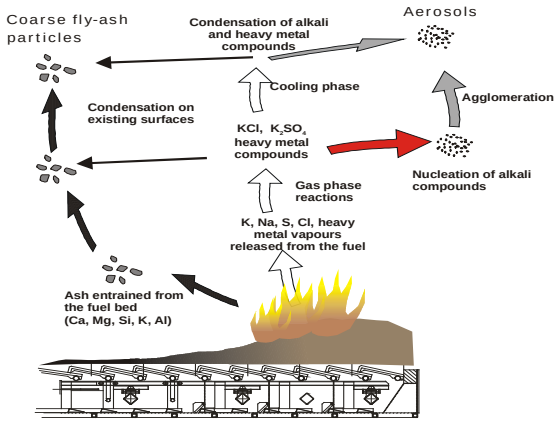



**Figure 8:** Mechanism of aerosol formation as suggested by [Christensen and Livbjerg, 1996; Christensen et al., 1998] for straw-fired systems and by [Brunner et al., 2000, 2002] for wood chips fired systems. Source: [Brunner et al., 2000, 2002].

The fine particles generated in biomass combustion are chemically characterised, mainly, by the elements K, Na, Cl, and S and are formed by condensation of volatile vapours [e.g. Christensen, 1995; Christensen and Livbjerg, 1996].

[Christensen et al., 1998] investigated aerosol formation during straw combustion. The aerosol particles sampled in full-scale consisted of KCl and $K_2SO_4$, with KCl being dominant, but $K_2SO_4$ being present in the core of the particles, see Figure 8. A quenched equilibrium theory by which the KCl, $K_2SO_4$, HCl, and $SO_2$ is determined by the equilibrium sulfation of KCl at 812 ± 10 °C, was used to quantify the chemical composition of the aerosol particles, and [HCl] and [$SO_2$] in the flue gas. The authors suggested that aerosol formation is initiated by homogeneous nucleation of $K_2SO_4$, particles then grow by heterogeneous condensation of $K_2SO_4$ and KCl.

Observations on aerosols formation during cooling of synthetic flue gas containing $KCl/O_2/H_2O/N_2$ in a laboratory reactor [Jensen et al., 2000] support the theory of [Christensen et al., 1998].

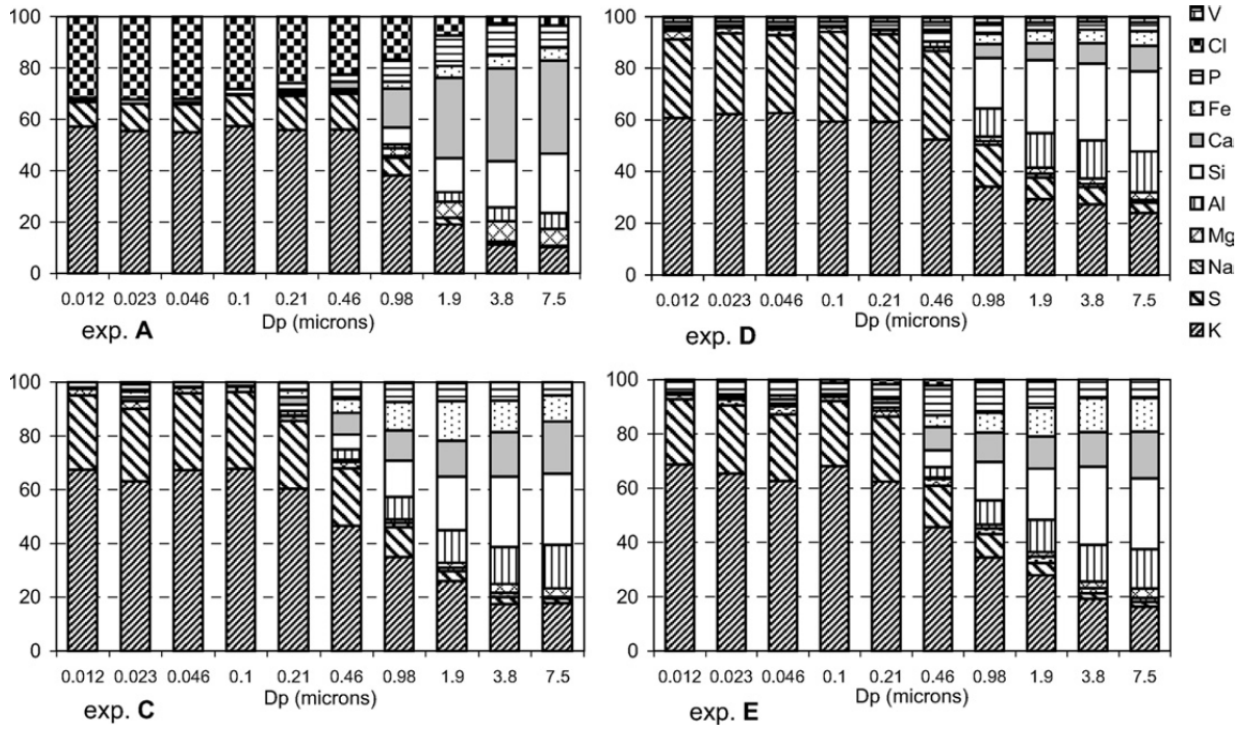



**Figure 9:** Elemental chemical composition (mass base) of particles on BLPI for experiments firing Orujillo alone (Exp. A) and Orujillo + coal at 1300 °C (Exp. C), Orujillo + coke (Exp. D) and Orujillo + coal at 1450 °C) (Exp. E). Source: [Jimenez and Ballester, 2005b].

For biomass and waste fractions other mechanisms seems to be of importance concerning aerosol formation, typically based on release of flame-volatile alkali or heavy metal species, which are subsequently supersaturated, before they can condense heterogeneously on the surface of entrained fly ash particles in the flue gas. One mechanism, suggested for aerosol

formation in straw-fired systems, proclaims that $K_2SO_4$ becomes supersaturated in the flue gas, forms nuclei, and subsequently grow by combined coagulation and heterogeneous condensation of KCl to form an aerosol [Christensen and Livbjerg, 2000].

Gas phase K-S-Cl chemistry and thereby aerosol formation may be seriously affected by the presence of additives. The influence of six additives; ammonium sulfate, monocalcium phosphate, Bentonite, ICA5000, clay, and chalk on aerosol formation was studied in a 100 $MW_{th}$ straw-fired boiler [Zeuthen et al., 2007b]. Bentonite and ICA5000 are mixtures of clay minerals consisting mainly of $Fe_2O_3$, $Al_2O_3$ and $SiO_2$. The experiments showed between 46 % and 70 % reduction in aerosol mass loading when adding ammonium sulfate, calcium phosphate, Bentonite, ICA5000, and clay, while addition of chalk increased the aerosol mass concentration by 24% [Zeuthen et al., 2007b]. Experiments in a laminar flow aerosol condenser with the same six additives showed reductions similar to the ones found in full-scale [Zeuthen, 2007].

As part of a study on particle formation during biomass combustion, the effect of combining biomass with other S-rich fuels (such as coal and coke) was investigated by [Jimenez and Ballester, 2005a]. Fine particles generated from combustion of pulverized olive residue (Orujillo) at 1300 °C and 5 % $O_2$ were composed of KCl and $K_2SO_4$ in almost equal mass proportions, See Figure X. When adding $SO_2$ as a pure doping gas (~180 ppmv) to the combustion gas, KCl disappeared from the fine particles, being substituted by more $K_2SO_4$. The same result was obtained when $SO_2$ was generated by co-firing of Orujillo and coal. The particle composition again revealed no presence of KCl for the higher $SO_2$ concentration (~400 ppmv) produced by co-combustion of Orujillo and coke, see Figure 9 [Jimenez and Ballester, 2005a]. These results agree with the aerosol formation mechanism proposed by [Christensen and Livbjerg, 1996], in which $K_2SO_4$ nucleates first, followed by heterogeneous condensation of KCl on existing particles.

In another study, the properties of fine particles from biomass combustion were experimentally investigated in an entrained flow reactor under a variety of combustion and post combustion conditions. The parameters varied include combustion temperature and the concentrations of oxygen and $SO_2$ in the flue gases. $SO_2$ was added as a pure gas or generated in co-firing experiments [Jimenez and Ballester, 2005b]. K, S, Cl, and P (in much smaller amounts) accounted for virtually all the mass in the submicron mode, mainly via binary mixtures of KCl and $K_2SO_4$ [Jimenez and Ballester, 2005b].

The amount of P in the submicron particles, increased strongly with combustion temperature above 1100 °C. [$SO_2$] and [$O_2$] in the flue gas control the final ratio of [Cl]/[$SO_4$] in the fine particles. Theoretical considerations based on a kinetic limitation in the formation of $SO_3$ from $SO_2$ by reaction with atomic oxygen were shown to be in good qualitative agreement with the measurements [Jimenez and Ballester, 2005b].

[Brunner et al., 2000, 2002] reported several test campaigns in a 440 $kW_{th}$ pilot-scale and a 40 $MW_{th}$ full-scale moving grate, utilizing wood chips (of spruce and beech), fibre board, bark and different types of waste wood. It was found that mass loading of coarse mode fly ash mainly depended on the ash content in the original fuel and the actual load of the combustion unit. With an increase in these parameters, particle entrainment from the fuel bed also increased.

The mass and chemical composition of aerosols was found to depend mainly on the feedstock chemistry. The higher the concentrations of K, Na, Zn and Pb, the higher the aerosol mass loading. Modeling and data from the test-runs, indicated that no other parameter (furnace temperature, load etc.) significantly influenced the mass of aerosols formed. Concerning the particle size distribution of aerosols, it was concluded that the time temperature – profile of the actual combustion unit may have a slight influence on the peak diameter of the resulting particle size distribution [Brunner et al., 2000, 2002].

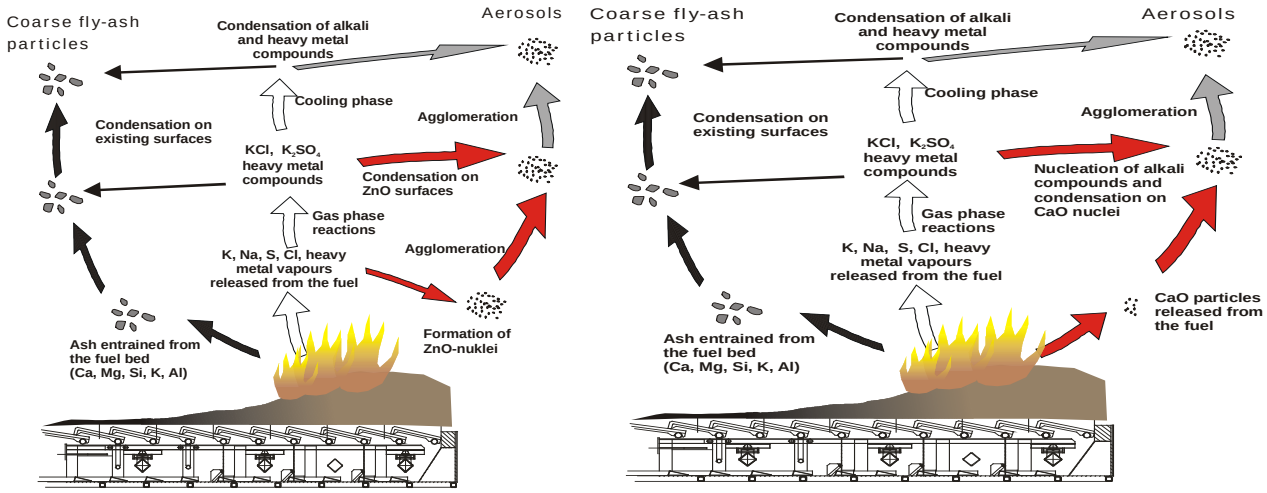



**Figure 10:** Basic mechanisms of aerosol formation from waste wood firing (left figure) respectively bark firing (right figure) as suggested by [Brunner et al., 2000, 2002].

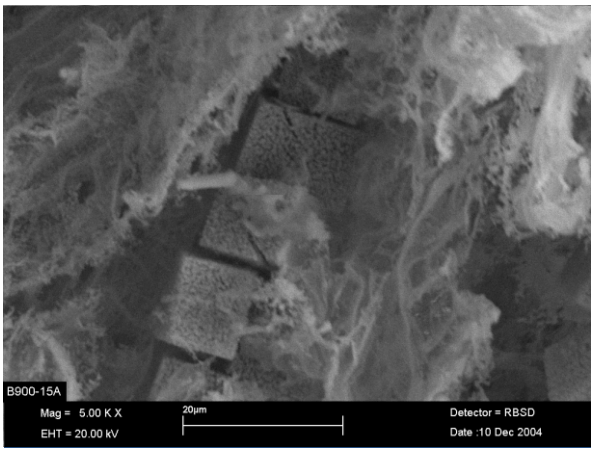



**Figure 11:** Chain of Ca oxalate crystals in partly pyrolyzed bark particle (900 °C, 15 minutes in air). It can be seen that the Ca oxalate particles have a grain-micrograin structure, i.e. the crystals are composed of much smaller lightly sintered particles rich in Ca [Frandsen et al., 2006].

Theoretical considerations and data from the test-runs lead to the proposal of three different aerosol formation mechanisms [Brunner et al., 2000, 2002];

- The first mechanism occurs when firing chemically untreated wood chips, where aerosol formation and growth are mainly due to nucleation and condensation of K-salts (KCl and $K_2SO_4$) followed by coagulation, see Figure 17. This formation mechanism is equal to the one proposed for aerosol formation in straw-fired plants;
- When firing waste wood, the behavior of Zn becomes important, see Figure 10. Under reducing conditions, elemental Zn is released [van Lith et al., 2006, 2008] to the gas phase. When re-oxidation takes place, ZnO(s) nuclei are formed. Eventually, further nucleation of alkali metal and heavy metal salts is suppressed by condensation on the large specific surface area provided by the high number of ZnO-nuclei, and subsequently particles grow due to condensation and coagulation.
- For bark, submicron particles based on a core of CaO was found, see Figure 10. It was initially argued that these CaO-nuclei are formed by a mechanism comparable to the reduction-reoxidation fume formation mechanism suggested for pc-fired units. Anyhow, although reducing conditions prevail in the primary combustion chamber, it is a question whether the temperature in this chamber is high enough to cause evaporation of Ca. In a subsequent study, it was shown that bark produces a lot of Ca oxalate crystals during pyrolysis and char oxidation, crystals with a distinct grain-micrograin structure, see Figure 11. It was then suggested that these Ca Oxalate crystals simply burst during the char oxidation, probably due to thermal tensions, and thereby form a fume of very small CaO-rich nuclei, which constitute the base for an aerosol to be formed. The CaO-rich particles do in most cases not provide enough surface area to suppress nucleation, meaning that K-salts still forms new particles. Subsequently, the CaO and K-salt particles grow by further heterogeneous condensation on their surfaces and by coagulation.

[Wiinikka et al., 2007] investigated the influence of fuel ash composition on aerosol formation during fixed bed combustion of woody biomass. Two wood pellets and one bark pellet type were investigated experimentally, in a 8 $kW_{th}$ updraft fired reactor, and theoretically, through chemical equilibrium modeling. The main conclusions were [Wiinikka et al., 2007];

- The particle mass size distribution in the $PM_{2.5}$ region was bimodal for all the pellets investigated;
- Early in the flame zone, the fine mode fraction from all pellets was dominated by particles from incomplete combustion (soot and/or other hydrocarbons), but these particles were subsequently oxidized in the hot $O_2$-rich flame;
- When the flue gas is cooled after the hot flame, inorganic vapor condenses and form particles, whereby the mass concentration and the particle diameter of the fine mode increase.
- The inorganic elements detected in the fine mode were K, Na, S, Cl, and Zn, for all pellets considered. For one of the wood pellets and the bark pellets, a significant amount of P was also detected in the fine mode. Alkali sulfates ($K_2SO_4$ and $Na_2SO_4$) and chlorides (KCl and NaCl) were formed from the inorganic vapour; the sulphates condense and form particles at a temperature of ~950 °C and alkali chlorides condense later at a temperature of ~600 °C (i.e. the same basic mechanism as suggested by [Christensen and Livbjerg, 1996]).
- For bark pellets, crystalline ZnO was found in the fine particles, while for the other two fuels the association of Zn could not be experimentally determined. This is abit

in contradiction to the data published by [Brunner etal., 2000, 2002] indicating Zn mainly in fine particles from waste wood combustion.

- For all pellets, the coarse mode in the $PM_{2.5}$ region consisted of carbon, refractory metals (Ca, Mg, Si, Mn, and Fe), and, considerable amounts of K, Na, S, Cl, Zn, and in some cases also P;
- The initial fuel alkali concentration and the (K + Na)/Si-ratio influenced the amount of vaporized aerosol forming matter in good agreement with the data published by [Knudsen, 2004; van Lith et al., 2006, 2008].

For fluid bed systems, aerosol mass loadings downstream the convective pass of a CFBC fired with willow (Salix) and forest residue were found to be 200 – 400 mg/$Nm^3$, while comparison of measurements upstream, in, and, downstream the convective pass, showed that a large mass fraction of super micron particles was deposited in the convective pass [Lind et al., 1997; Lind, 1999; Valmari et al., 1998]. Mass size distributions were bi-modal both upstream and downstream of the convective pass; the size of the fine mode particles was in the range [0.1 – 0.6 μm] while that of the coarse mode was [1 – 100 μm] [Johansson, 2002]. Submicron particles sampled upstream of the convective pass [830 °C] during combustion of forest residue were found to be composed of $K_2SO_4$ and KCl, with the presence of some Ca and Na, also. Downstream of the convective pass [160 °C] of the boiler, the particles less than 0.5 μm mainly consisted mainly of KCl [Lind, 1999]. The coarse particles formed from the non-volatilized ash residue contained the elements Ca, K, P, Mg, and S.

| **Fuel\Technology** | **Suspension-firing** | **Fixed-bed firing** | **Fluid-bed firing** |
|---|---|---|---|
| **Coal** | ☺☺☺☺ [1,2] | *Of minor relevance* | ☺ |
| **Annual biomass/ Energy Crops** | ☺☺ [3] | ☺☺☺☺ [4] | ☺☺ [5] |
| **Wood fuels** | ☹ | ☺☺☺☺ [6] | ☺☺☺ [7] |
| **Waste fractions** | ☺ | ☺ | ☹ |

**Table 2:** Overview of available data on aerosol formation when firing different fuels in different technologies. A lot of chemical and size distribution data as well as mechanisms of aerosol formation is available for coal firing in suspension, straw firing on grates and wood firing on grates and in FBCs.
1,2 – [Quann and Sarofim, 1982; Helble and Sarofim, 1989a], 3 – Basic study conducted at MKS1 [Andersen, 1998], 4 – [Christensen and Livbjerg, 1996], 4 – [Christensen and Livbjerg, 1996; Christensen et al., 1998], 5,7 – [Lind et al., 1997, 1999; Valmari et al., 1998], 6 - [Brunner et al., 2000, 2002].

A very important step in the formation of aerosols by sulfate super saturation is the sulfation reaction, causing formation of the $K_2SO_4/Na_2SO_4$. Several studies have been conducted in order to outline gas phase alkali-S-Cl chemistry as a function of S/Cl-ratio, temperature etc. It is still a question open for discussion, whether the sulfation reaction goes on homogeneously or heterogeneously [Frandsen, 2011].

To sum up, a lot of chemical and size distribution data, as well as mechanisms of aerosol formation are available for coal firing in suspension, straw and wood firing on grates, and in FBCs. At present we have a really good understanding of how aerosols are formed in these

systems, and, what the emission and operational consequences are of this. For some of the other combinations of fuels and technologies, a full mapping of aerosol formation is still on its way.

There is a gap in the basic data available on, and the understanding of aerosol formation, in co-fired systems, maybe with exception of coal-straw co-firing, where [Nielsen et al., 1996] set the standard. Further, the synergetic effect of blending fuels on aerosol formation and behavior needs more systematic attention. So does aerosol formation from waste-firing in FBC and the effect of wood on aerosol formation in systems co-fired with wood and coal in suspension [Frandsen et al., 2010].

## 4. RESIDUAL ASH FORMATION

Most of our current knowledge on fly ash formation originates from PC-firing. As a coal particle is being heated, it may physically break up into fragments, due to the thermal stresses, induced by internal fissures, cracks, and structural imperfections initially present. Volatile fractions originally present in the coal or formed by pyrolysis are vaporized, and the particle may burst open from the internal evolution of such gases. Further, a heated coal particle may swell and become more porous. As the particle burns, pores in the carbon matrix open and the porosity increases further. Ultimately, the particle becomes so porous, that it disintegrates into a number of fragments, each of which may contain a fraction of the mineral matter, that was present in the original coal particle [Beer et al., 1992; Boni et al., 1990; Flagan and Friedlander, 1978].

Studies of the evolution of ash during pulverized coal combustion, have revealed that ash remaining in the condensed phase during carbon burnout, account for most of the mineral matter in the raw coal. As carbon is consumed, mineral inclusions come into contact with one another, forming larger ash clusters, which coalesce to form large ash droplets on the surface of the burning char. The fragmentation of char limits the degree of coalescence of ash inclusions within a single coal particle [Senior and Flagan, 1982; Flagan and Seinfeld, 1988].

[Helble and Sarofim, 1989b] investigated the influence of char fragmentation on the size distribution of fly ash in a detailed lab-scale study, utilizing both coals and synthetic chars. Combustion of three different coal types, resulted in production of ash particles in the size range 1 – 10 μm, at all conditions considered (1230 °C and 1480 °C, 8 % $O_2$ and higher). The amount of ash in the 1 – 5 μm range was found to be relatively invariant with combustion conditions, and typically constituted 10 – 20 % of the total ash mass, which greatly exceeds the mass predicted from a model assuming that one ash particle is produced per char particle. The macroscopy of the char was found to be the main variable in determining fragmentation behavior, as evidenced by results from combustion of synthetic chars; macro-porous Spherocarb doped with Na-silicate, produced 75 ash particles greater than 1 μm in diameter per char particle, while non-macro porous sucrose/carbon black chars doped with Na-silicate, yielded only 1 ash particle per char particle [Helble and Sarofim, 1989b].

Laboratory experiments have shown that, typically, 3-4 residual fly ash particles are formed per coal particle [Helble, 1987; Sarofim and Helble, 1994].

Theoretically, the formation of residual fly ash in pc-fired boilers, may be described by two extremes:

1. No coalescence i.e. each mineral grain creates a single fly ash particle with a chemical composition equal to the decomposition phase of the mineral, and;
2. Full coalescence where all the mineral grains in a coal particle fuses together and create a single fly ash particle with a chemical composition equal to the average composition of the decomposition phases of all the mineral grains.

The full coalescence limit is also known as the shrinking sphere model for coal combustion. A mathematical model for fly ash formation, based on those two limits was presented by [Charon et al., 1990].

The following conclusions were drawn by [Korbee et al., 2010] on ash formation during suspension-firing of biomass:

- The ash transformations and char combustion, was in the kinetic-diffusion controlled regime, even with extended residence time under typical pulverized fuel firing conditions.
- Char chemical conversion was found to be dependent on the ash and the volatile matter contents, at typical pulverized fuel firing conditions. Fuels having high ash content, formed fewer active carbon sites for smooth char oxidation, and were therefore converted more slowly. This was observed for the Polish coal, the UK coal, and to a lesser extent the olive residue and the straw. The Polish and the UK coals were further characterized by high ash and low volatile matter contents. Therefore, the overall chemical conversion is lower for both of these fossil fuels. On the contrary, the olive residue and the straw have relatively high shares of volatile matter. Therefore, the initially slow conversion was quickly accelerated when fuels reach a certain critical temperature. The high volatiles result in a high overall conversion. Also, smaller size particles converted more quickly than higher size particles.
- Devolatilization of the fuels also depended on the mineral matter, and its association with the carbon-matrix. Fuels rich in volatile matter were found to be devolatilizing quickly, and to a high degree. Chlorine and sulfur started devolatilizing early on in the combustion process. Alkalis release will be limited, in the presence of silicon and aluminum in the fuel. Other more conservative oxides such as those of calcium and magnesium, were also found to be devolatilizing in some of the fuels, where their content is high.
- Fragmentation was found to be dependent on the overall fuel chemical conversion and devolatilization. The quicker and the higher the fuel chemical conversion and the devolatilization, the more pronounced will be the fragmentation. Woody biomass was a good example of this mechanism. Three kinds of fragmentations were observed: attrition, breakage, and percolative fragmentation. During the initial heat up and devolatilization, biomass and coalwere found to be fragmenting attritively. Percolative fragmentation was observed, only after a critical conversion of the char (approximately 60-70%). Bigger particles fragmented more than small ones.
- Although the present study does not include the effect of the particle size, its shape, density, and the mineralogy (included/excluded minerals), at the given operating conditions, qualitative predictions based on the fuels mineral matter elemental

composition, as well as the volatile matter contents, appear to match with the experimental results very closely.

[Damø et al., 2014, 2017] tried to deduce the physical mechanisms of fly ash formation from biomass fired in suspension. The overall objective of the work was to generate novel and comprehensive data on the formation of residual fly ash during the initial stage (0,25 – 2 s) of suspension-firing of biomass (pulverized wood and straw). Combustion experiments were therefore carried out with bio-dust (pulverized straw and wood), in a pilot-scale entrained flow reactor, simulating full-scale suspension-firing of biomass. By the use of a movable, cooled and quenched gas/ particle sampling probe, samples were collected at different positions along the vertical axis in the reactor, corresponding to gas residence times, varying in the range [0,2 – 2 s]. The collected particles were subjected to various analyses, including light-scattering technique (Malvern Mastersizer) for determination of particle size distribution, bulk chemical analysis (ICP-EOS) for elemental composition, SEM/EDS analysis for investigation of particle morphology and composition, and STA-analysis for determination of carbon/char burn-out level.

The ash formation mechanisms were found to be quite similar for both straw and wood, in the sense that [Damø et al., 2014, 2017]:

- Within the initial 0.25 – 0.28s after the fuels are injected into the hot zone (≥ 1200 °C) of the reactor, the flame volatile inorganic elements, K, Cl and S, are released to the gas phase, to a significant extent. The degree of char burn-out at this point was in the range 72 – 91 %. Some of the smaller sized fuel particles had been fully converted to ash at this point, but char particles with a size ≥ 50μm, and with a significant content of organic matter, was by far the largest contributor to the PSD.
- At 1.0 - 1.1s of residence time, char burn out, mineral particle fragmentation and ash particle melting had taken place, which was reflected in the PSD as the evolution of a new, intermediate-sized (fragmentation-mode) peak with maximum dp around 30 – 50 μm, while the concentration of larger particles above 200 – 300 μm is fading. The particles in the intermediate-sized interval appeared in SEM, as a mixture of spherical and irregular fly ash particles, and some char fragments. The char and ash particles were more or less covered with smaller ash particles/droplets, originating partly from coalescence of ash droplets on the receding char surface, and, partly from condensation of salt species on the particles during the cooling process.
- At 1.7 – 2.0s of residence time, the PSD is further developed. However, in most cases some organic matter was still present in the ashes at 1.7 s / 2.0s, indicating that further development of the PSD may occur at longer residence times. In the wood ashes in particular, char particles with some of the original wood structure preserved were abundant, even after 1.7 – 2.0s of conversion. After cooling of the flue gas, submicron aerosol particles, consisting primarily of KCl, were now abundant in the ashes from straw combustion, and aggregates of the submicron aerosol particles were covering the surface of several of the larger fly ash particles.

For all ashes at long residence times, a peak of ash particles were observed in the range of 20 to 100 μm. Release of K to the gas phase were nearly 100 % for straw and the wood samples. A straw sample with high Si/K content, showed a release of K in the range of 65 %. All S and Cl was nearly completely released to the gas phase, for all studied samples.

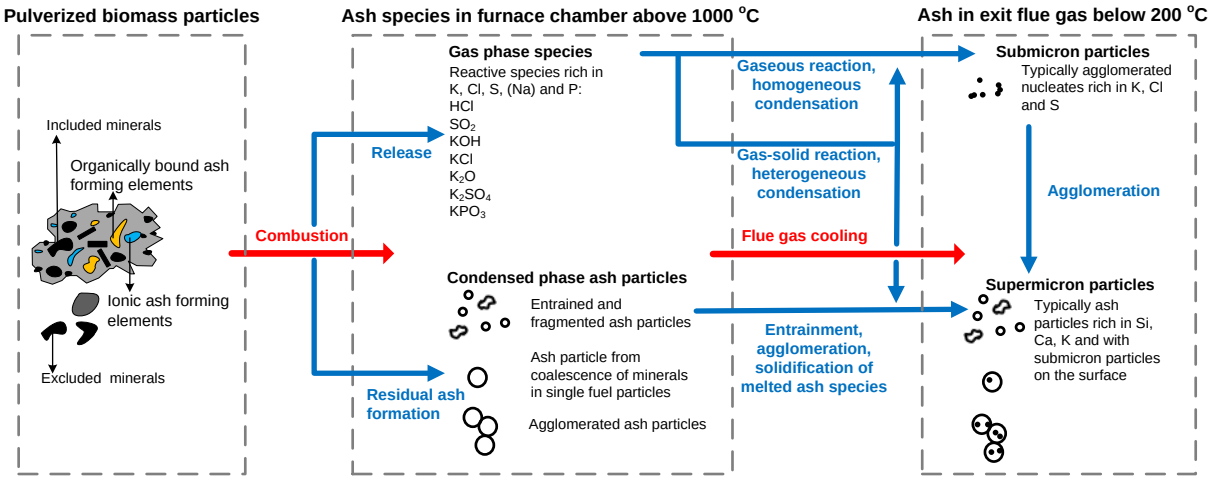



**Figure 12:** Major transformation routes and transformation processes for ash forming elements during biomass suspension-firing. Source: [Damø et al., 2017].

Based on their work, and the existing literature in the field, [Damø et al., 2014, 2016] suggested major transformation routes and transformation processes for ash forming elements, during biomass suspension-firing, see Figure 12.

For grate-firing of biomass, [Frandsen et al., 2006] combusted spruce and bark samples have been in a lab-scale reactor, at temperatures of 700, 800, and 900 °C, different $O_2$-levels (2.5 %(v/v) and 21 %(v/v)), and in different time ranges (pyrolysis in $N_2$, and pyrolysis followed by 5, 15, respectively 30 minutes combustion in access to oxygen), in order to investigate the formation of residual ash on the surface of the resulting char particles.

Extensive SEM/EDX-analysis showed surface enrichment of K, Ca, Mg, P and Mn along the residual ash/char samples, from both spruce and bark. The surface enrichment occurs during pyrolysis, and in the early stages of the char burnout, due to decomposition of polymers in the wood structure. As the organic matrix is degraded, the surface enrichment becomes more distinct, and the ash-forming elements are revealed from the decomposing fibres [Pedersen, 2003; Frandsen et al., 2006].

It was concluded that residual ash formation mainly depends on the amount and association of ash-forming elements, which will determine the degree of interactions of the residual ash, but also on the actual temperature on the grate, the mixing between fuel and oxidizer (access to oxygen), and the total time available for thermal conversion to occur [Frandsen et al., 2006].

Thus, for coal-firing in suspension a lot of high-quality, pioneering work have been conducted in several places in the USA, including first and foremost MIT, but also University of Arizona, and University of Kentucky. Imperial College in the UK, and, ECN in the Netherlands, have also contributed to the current state of knowledge. The basic mechanism of fly ash formation in pc-fired boilers is well described, documented and may even be modeled relatively precisely. Concerning fly ash formation from biomass or waste fractions, the situation is not nearly as good. Lots of data are available from campaigns where different

ash fractions, including sometimes also in-situ ash, have been collected and analyzed chemically. So there is a good basic understanding of the chemistry of fly ash formed in plants fired with biomass or waste fractions, either alone or in conjunction with coal. But data on dedicated studies of the physical size development of fly ash are scarce for biomasses and waste fractions. A lot of further work is needed on this subject, before we can predict the chemical composition and size distribution of a fly ash from any of these fuels.

| Fuel\Technology | Suspension-firing | Fixed-bed firing | Fluid-bed firing |
|---|---|---|---|
| **Coal** | ☺☺☺☺ [1] | *Of minor relevance* | ☺☺ |
| **Annual biomass/ Energy Crops** | ☺ [2] | ☹ | ☹ |
| **Wood fuels** | ☺ | ☺ [3] | ☺ [4] |
| **Waste fractions** | ☹ | ☹ | ☹ |

**Table 3:** Overview of available data on residual ash formation when firing different fuels in different technologies. The mechanism of residual ash formation is very well described for coal-firing in suspension, while there are serious gaps in the current understanding of residual ash formation when utilizing annual biomass/energy crops, wood fuels and waste fractions in basically all technologies.
1 - [Helble and Sarofim, 1989b], 2 – Basic study conducted at MKS1 [Andersen, 1998], 3 - [Brunner et al., 2000, 2002], 4 – [Lind et al., 1997, 1999; Valmari et al., 1998].

## 5. SUMMARY/SUGGESTIONS TO FURTHER WORK

The inorganic fraction (in-combustibles) of a fuel undergoes several complex chemical and physical transformations during devolatilization/pyrolysis, and char burnout, see Figure 26. Intermediate ash species including gases, liquids, and solids are formed, and the size and composition of these affects their subsequent fate in the combustion system.

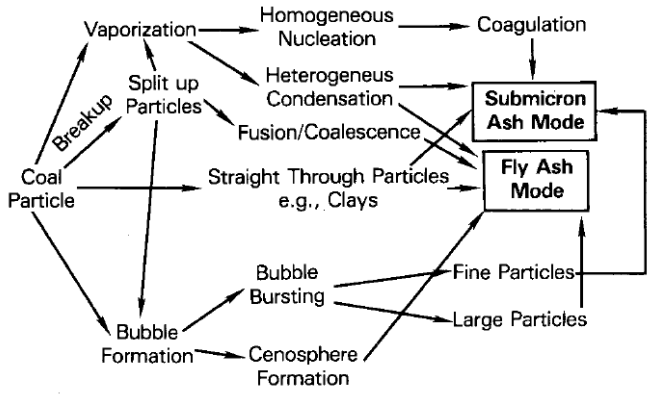



**Figure 13:** Chemical and physical processes controlling formation of the submicron ash mode respectively the fly ash mode when firing pulverized coal. Source: [Damle et al., 1982].

If we want a detailed understanding and a mechanistic prediction of deposition, based on data available before the fuel is combusted, we need strong focus on deriving mechanisms of residual ash formation especially from secondary fuels like low-rank coals, biomass and

waste. The entrainment, transport and thereby depositional behavior as well as potential as acting as a drain for condensable gaseous species from the flue gas, during cooling from the furnace to the particulate removal device, links strongly to the actual physical size distribution of the fly ash particles. Thus, the physical development of residual ash link to its fate further down the line in the actual combustion system;

- Will it be lifted from the fuel-bed/flame up through the freeboard ?
- How will it transform and/or interact with e.g. gaseous species during transport up through the freeboard etc. ?
- Will it be transported to the heat transfer surfaces, and in case yes, where in the system will that happen ?
- Will it stick to the heat transfer surface upon impact ?

The main parameters controlling release of the critical elements (i.e. Na, K, S, Cl, P, Cu, Pb, Zn) and formation of the residue (fly ash) during thermal conversion of a fuel, are;

- The conversion temperature (in the range 500 – 1500 °C)
- The residence time (from ms to several minutes)
- The stoichiometry: pyrolysis/combustion/gasification (i.e. access to oxygen)
- The design of the actual system: burner (suspension firing) vs. fixed bed (grate firing). This determines the fuel-oxidizer contact pattern
- The fuel particle size (in between a few μm and several mm)

In addition to these parameters fuel type (biomass, waste fractions, coal), ash content, chemical composition and association of inorganic elements (organic vs. inorganic) also plays a major role for the ash formation process.

This paper has been divided into three main sections, dealing with release of critical elements like K, Na, S, Cl, Zn and Pb, formation of aerosols and residual ash;

- There are a lot of high-quality data available on the release of critical elements, although most of the lab-scale measurements are performed under conditions different from what really happens in full-scale. The main difference being the particle size distribution of the fuels investigated and the time-temperature history, mainly the heat-up rate. Nevertheless, the data are available and several good attempts have been made to derive mechanisms for the release of especially K, S and Cl, taking into account chemical interactions with other elements like Al, Si, Ca and P. But the fact is that there is still a big gap to fill out before we have a reasonable modeling of the release from single particles and beds of burning fuels. Thus, we are still by no means able to provide reliable boundary conditions for e.g. advanced flow models to simulate freeboard chemistry etc. in these systems.
- At lot of focus has been but on aerosol formation when utilizing solid fuels, in the entire range of fuel qualities from coal, via wood fuels to annual biomasses and waste fractions. The fundamental aspects of aerosol formation from these fuels have been outlined via a significant number of measuring campaign. We have a good qualitative image of the mechanisms of aerosol formation for most of the fuels and in some cases reliable 1st generation models for aerosols formation have been suggested, especially for coal-firing in suspension and straw-firing on a grate. Aspects of aerosol transport

are also addressed thoroughly in the literature. Anyhow, there is also here a big gap to step over before these models are fully implemented in e.g. models for freeboard chemistry or advanced flow in furnaces.

- The last leg is fly ash formation, which is well described for coal-firing in suspension, where reliable models for prediction of chemistry and particle size distribution have been published and tested in the literature. For utilization of many of the other fuels, the physical description of how fly ash is formed is almost non-existing. The physical development of fly ash link to its fate further down the line in the actual combustion system; will it be lifted from the fuel-bed ?; how will it transform and/or interact with e.g. gaseous species during transport up through the freeboard etc. ? will it be transported to the heat transfer surfaces, and in case yes, where will that happen ?; will it stick to the heat transfer surface upon impact ? Often, we have lots of chemical analyses of residual ash particles that have been collected in various positions when utilizing these fuels, but there is an almost complete lack of physical understanding and investigations in this area. How do these particles develop physically during the thermal fuel conversion process and what mechanisms are controlling this ? This will affect their size distribution and chemical composition.

Thus, there are still several gaps in our understanding of release and formation of aerosols and fly ash, in spite of 30+ years of high quality research on these issues.

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